MONITORING OF CHLORINE IN COAL DURING PYROLYSIS BY SIMULTANEOUS TG/FTIR TECHNIQUE

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INTRODUCTION

At least half of the known economically minable coal resources in Illinois have a high chlorine content (>0.3%). Coal with such high chlorine content may be difficult to market because the chlorine may not only enhance boiler corrosion rate of metal tube walls in utility and industrial boilers, but also contribute to environmental pollution. However, assessing the effect of chlorine in coal on boiler corrosion is a complex problem. There are many variables which may synergistically affect the corrosion rate in a boiler, and there is a lack of data to isolate individual factors.

Boiler corrosion is controlled by several other factors, in addition to the chlorine content, including temperature, oxidizing-reducing conditions, alkali contents, sulfur content, and ash composition. For several decades, chlorine-enhanced corrosion has been attributed to the presence of chloride which prevents the formation of a protective layer of oxides on metal surfaces. Direct HCl attack is also a potential corrosion mechanism. Chlorine-enhanced corrosion is believed to be more significant under a reducing condition than an oxidizing condition. Under the oxidizing condition, the metal surface is coated with a protective oxide layer, and corrosion is constrained by diffusion of corrosive gaseous species through the protective layer. In contrast, under the reducing condition the deposits on mental surfaces are a mixture of oxides and sulfides, which do not form as good a protective layer as compact oxides. Thus, corrosion can be significant in areas under a reducing atmosphere. The mechanism of boiler corrosion is related to the relative abundances of gaseous species (HCl, NaCl, KCl, Cl_2, SO_2, H_2S, etc.) in combustion gases, which in turn are related to the composition of feed coal and combustion conditions.

Several studies have been done on the behavior of chlorine in the British coal during pyrolysis/combustion. Edgecombe concluded that chlorine in the British coals was liberated as HCl gas only in air at 200^0C, whereas Daybell concluded that chlorine in the coals was liberated as HCl gas also in oxygen-free nitrogen at 200^0C.

Gibb concluded, however, that the British coals gave off 97% of its chlorine as HCl gas in oxygen-free nitrogen at 258^{0}C. There is a lack of data concerning the behavior of chlorine in the Illinois coals during pyrolysis/combustion.

This study is part of an on-going the project: Behavior of Sulfur and Chlorine in Coal during Combustion and Boiler Corrosion. One important purpose of this project is to determine the gaseous species in pyrolysis/combustion gases and the kinetics of their release during pyrolysis/combustion. The results will lead to a better understanding of the relation between the chlorine and alkali levels in feed coal and boiler corrosion can be better understood. The purposes of this study were to identify HCl gas from the gaseous species evolved from the Illinois coals and to observe the behavior of chlorine in the coals during pyrolysis by using the simultaneous TG-FTIR techniques. We also tried to establish the relation between the amount of chlorine liberated as HCl gas and temperature.

EXPERIMENTAL PROCEDURES

Samples

Two coal samples from the Illinois Basin Coal Sample Program were used in the experiments: IBC-109 (0.42% chlorine, 1.13% sulfur) and IBC-106 (0.02% chlorine, 3.77% sulfur).

Identification of gaseous chlorine species in pyrolysis gas and determination of gas release profile using thermal gravimetry (TG) in conjunction with Fourier transform infrared spectroscopy (FTIR).

Using the TG-FTIR system , the gases produced on a DuPont-951 TGA are analyzed by FTIR spectroscopy using the Perkin Elmer-1650 FTIR spectrometer. Thermogravimetry provides a means for measurement of heating condition and weight change. The system is able to continuously monitor the weight change of a coal sample as well as to quantitatively determine the gases evolved (CO, CO_2, COS, SO_2, HCl, H_2O, NO, NO_2, NH_3, CH_4, C_2H_4, C_3H_6, etc.) during pyrolysis. The TGA furnace is connected to the 100 x 24 mm gas cell through a 1-mm Teflon tube. Both the Teflon line and the gas cell can be heated by heating coils up to 250^{0}C. The time lag between the sample and the gas cell is one minute with a gas flow of 50 ml/min; the spectrum can be taken every minute. This also includes the time it takes to store the spectrum on the computer. Calibration of the FTIR is made using pure gases or prepared gas mixtures.

Approximately 100 mg of coal was used in each TG-FTIR experiment. The pyrolysis was conducted with a nitrogen gas (flow rate 50 ml/min), a temperature program from ambient to 900^{0}C, a heating rate of 10^{0}C/min. The FTIR scanning period was four seconds.

Determination of gaseous chlorine release profile using ion chromatography (IC)

Several filtering test tubes with gas dispersers were connected in a series with TG-FTIR to collect the pyrolysis gases in different temperature ranges; three trapping solutions connected in a series were used for each temperature range. The HCl vapor was trapped in 90 ml of 0.01% sodium carbonate solution and the solution was diluted to 100 ml. The solution was analyzed for chlorine concentraton by the Shumadzu HIC-6A ion chromatographic system.

RESULTS AND DISCUSSION

TG/DTG Analysis

The thermogravimetric curves obtained from the pyrolysis of samples IBC-109 and IBC-106 are shown in Figure 1. The temperature of the maximum rate of weight loss (T_{max}), % weight loss, and the maximum rate of the weight loss (R_{max}) in %/min are list in Table 1. Two samples have similar curves of weight loss and weight-loss rate, but their amounts of weight loss and rates of weight loss are slightly different. Weight loss occurred in two major temperature ranges: between 20^0 and 150^0C and between 350^0 and 850^0C. In the 20^0 - 150^0C range, IBC-109 had a weight loss of 4.23%, and IBC-106 6.4% as a result of the loss moisture. The second weight loss occurred in the temperature range of 350^0 - 850^0C, IBC-109 had a weight loss of 26.1% and IBC-106 32.3%. These weight losses correspond to the loss of the volatile matter, and are comparable to the volatile matter content of the coals determined with Leco MAC-400 analyzer (32.0% of IBC-109 and of 35.9% of IBC-106 on an as-received basis).

Table 1. Results of TG/DTG analysis on coal samples IBC-109 and IBC-106.

Sample	Temp.Range	T_{max}	Weight Loss	R_{max}
IBC-109	20.0^0-149.8^0C	87.1^0C	4.2 %	0.56 %/min
	149.8^0-351.0^0C		1.7 %	
	351.0^0-889.7^0C	450.5^0C	26.1 %	1.26 %/min
IBC-106	20.0^0-150.0^0C	87.1^0C	6.4 %	0.85 %/min
	150.0^0-348.7^0C		1.5 %	
	348.7^0-833.1^0C	422.5^0C	32.3 %	2.71 %/min

FTIR Analysis

The gases evolved from coal during pyrolysis were identified by FTIR spectroscopy. In order to identify the evolved gases, we analyzed some of the pure gases by FTIR, which were suspected to be present in the evolved coal gases . Figure 2 shows the standard

FTIR spectra of the pure gases (HCl, SO_2, CO, CO_2, H_2O and CH_4). The data of FTIR for the rest of the evolved gases were taken from the literature. Figure 3 shows the FTIR spectra of two samples at about 490^{0}C. The volatile species identified include carbon dioxide (CO_2,2360 cm^{-1}), carbon monoxide (CO, 2175 CO cm^{-1}), sulfur dioxide (SO_2, 1360 cm^{-1}), carbon oxide sulfide (COS, 2072 cm^{-1}), water moisture (H_2O, 1683 cm^{-1}), ammonia (NH_3, 966 cm^{-1}), hydrogen cyanide (HCN, 713 cm^{-1}), nitrogen monoxide (NO, 2050 cm^{-1}), nitrogen dioxide (NO_2, 1468 cm^{-1}), methane (CH_4, 1304 cm^{-1}), ethylene (C_2H_4, 950 cm^{-1}), propylene (C_3H_6, cm^{-1}), and hydrogen chloride (HCl, 2962 cm^{-1}).

The gas release profiles from coal IBC-109 determined by TG-FTIR analysis are shown in Figure 4-1 and 4-2, respectively, and those for sample IBC-106 are shown in Figure 5-1 and 5-2, respectively. A quantitative identification of HCl, however, is not straightforward because both CH_4 and HCl absorb around 2962 cm^{-1}. In order to resolve the contribution of each gas to the peak at 2962 cm^{-1}, the standard FTIR spectra of pure HCl and CH_4 were analyzed (Figure 6). Absorption peaks of methane occur in two regions: region I with wavenumbers from 3207 to 2679 cm^{-1}, and region II from 1392 to 2679 cm^{-1}. So the absorption peaks of HCl overlap completely with the peaks in the region I of CH_4.

In determining CH_4 gas, some peaks in region II (such as 1304 or 1269 cm^{-1}) can be used; the CH_4 release profiles (peak absorbance intensity vs. temperature) for IBC-109 and IBC-106 are shown in Figures 7 and 8, respectively. The gas release profile of HCl may be established as described in the following. First, the behavior of the peaks in region I where peaks of CH_4 and HCl overlap may be compared with the peaks in region II (CH_4). The gas release profiles of IBC-109 are shown in Figure 7 for the 1304 cm^{-1} and 1269 cm^{-1} peaks from region II (CH_4), and the 2962 cm^{-1} peak from region I(CH_4 + HCl). Both profiles of 1304 cm^{-1} and 1269 cm^{-1} (CH_4) have a peak at 550^{0}C with different intensities. In contrast, the profile of 2962 cm^{-1} (HCl + CH_4) has a peak at 490^{0}C. This temperature is significantly lower than the 550^{0}C peaks of CH_4. Thus, the 490^{0}C peak of 2962 cm^{-1} is mainly due to HCl, with a limited component of CH_4. Furthermore, the intensity ratio between the 2962 cm^{-1} and 1304 cm^{-1} peaks of the high-chlorine coal IBC-109 (0.42%) is 0.67; this is much larger than a ratio of 0.30 for the low-chlorine coal IBC-106 (Figure 8). Hence, the higher intensity of the 2962 cm^{-1} peak of IBC-109 is caused by its higher chlorine content (0.42%) than that of IBC-106 (0.02%). The HCl release profile may be obtained by subtracting the CH_4 component from the profile of 2962 cm^{-1}. The resulting profile should be close to that of curve (b) in Figure 8. The HCl gas appears to be released between 300^0 and 700^{0}C with a peak slightly below 490^{0}C during pyrolysis.

Determination of Chlorine in Pyrolysis Gas by Ion Chromatography

Trapped in the sodium carbonate solution, the chlorine released in each temperature range during pyrolysis of the high-chlorine coal IBC-109 was determined quantitatively by ion chromatography (IC). The data are summarized in Table II and the chlorine release profile is shown in Figure 9. The IC analysis indicates that the gaseous chlorine (mainly due to the HCl gas) is released mainly between 250^0 and 700^{0}C with a peak in the 450^0 - 500^{0}C range, and about 90% of chlorine in the coal was evolved during pyrolysis.

Table II. Results of determination of gaseous chlorine released in different temperature ranges by IC analysis.

Temp Range(^{0}C)	Amount of Cl(ug)	%Cl vs. Total Cl
100 - 250	19.95	4.75 %
250 - 300	28.30	6.74 %
300 - 350	40.02	9.53 %
350 - 400	43.19	10.28 %
400 - 450	47.05	11.20 %
450 - 500	47.42	11.29 %
500 - 550	41.87	9.97 %
550 - 600	41.33	9.84 %
600 - 650	40.70	9.69 %
650 - 700	29.88	7.11 %
Total	379.90	90.45 %

CONCLUSIONS

The pyrolysis-thermogravimetry-Fourier transform infrared (TG-FTIR) analysis was carried out on two coal samples: the high-chlorine coal IBC-109 and the low-chlorine IBC-106: The volatile species identified by the FTIR spectroscopy include CO_2, CO, NO, NO_2, NH_3, HCN, SO_2, COS, H_2O, CH_4, C_2H_4, C_3H_6, and HCl. The absorption peaks of HCl overlap with those of CH_4. However, the 2962 cm^{-1} peak is mainly due to HCl because this peak is stronger for the high-chlorine coal IBC-109 than that of the low-chlorine coal IBC-106. The gas release profile of 2962 cm^{-1} has a peak at 490^{0}C, significantly lower than that of wavenumber 1304 cm^{-1} (CH_4). We will obtain the HCl release profile by subtracting the CH_4 component from the from the 2962 cm^{-1} profile following appropriate calibration. The resulting profile should be close to curve (b) of Figure 8. It appears that HCl the high-chlorine coal was evolved between 300^0 and 700^{0}C with a peak slightly below 490^{0}C during pyrolysis. This was consistent with the results obtained by IC analysis.

ACKNOWLEDGEMENTS

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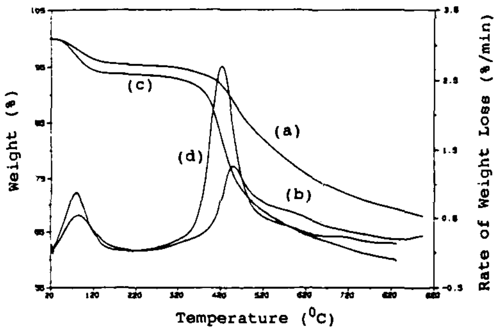

Figure 1. The thermogravimetric curves of coals IBC-109 and IBC-106. (a) TG curve of IBC-109, (b) DTG curve of IBC-109, (c) TG curve of IBC-106, and (d) DTG curve of IBC-106.

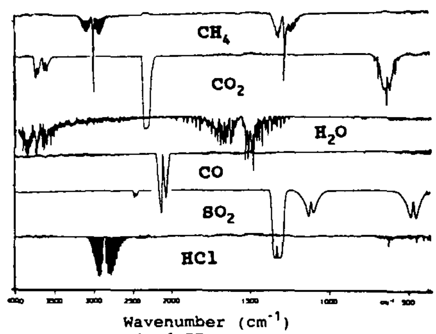

Figure 2. Standard FTIR spectra of some pure gases.

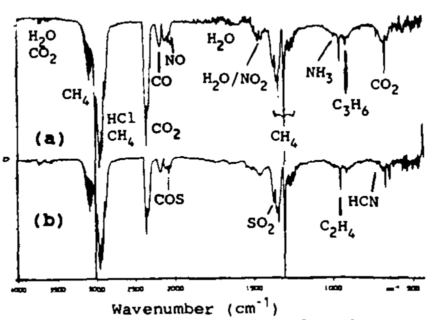

Figure 3. The TG-FTIR spectra of coals IBC-109 and IBC-106. (a) IBC-109 at about 490^{0}C, (b) IBC-106 at about 490^{0}C.

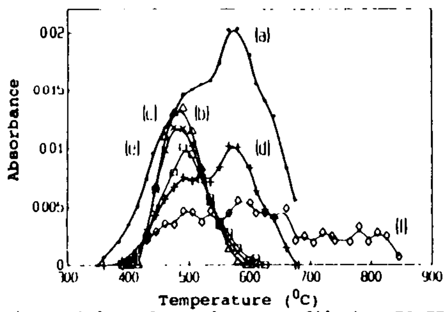

Figure 4-1. Gas release profile by TG-FTIR analysis for the high-chlorine coal IBC-109. (a) COS (2072 cm^{-1}), (b) NO_2/H_2O (1468 cm^{-1}), (c) H_2O (1683 cm^{-1}), (d) NO (2050 cm^{-1}), (e) NH_3 (966 cm^{-1}), and (f) HCN (713 cm^{-1}).

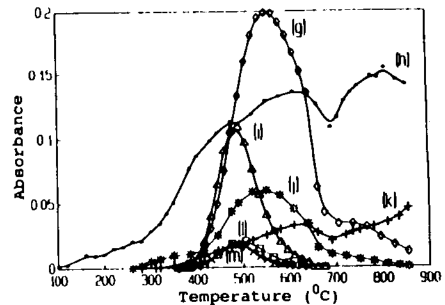

Figure 4-2. Gas release profile by TG-FTIR analysis for the high-chlorine coal IBC-109. (g) CH_4 (1304 cm^{-1}), (h) CO_2 (2360 cm^{-1}), (i) HCl/CH_4 (2962 cm^{-1}), (j) SO_2 (1360 cm^{-1}), (k) CO (2175 cm^{-1}), (l) C_2H_4 (950 cm^{-1}), and (m) C_3H_6 (912 cm^{-1}).

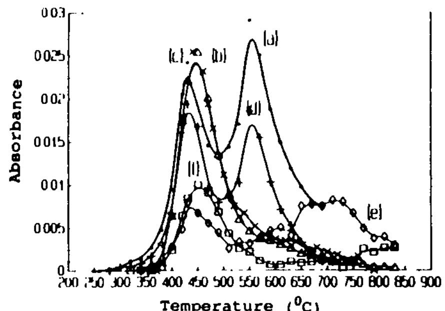

Figure 5-1. Gas release profile by TG-FTIR analysis for the low-chlorine coal IBC-106. (a) COS (2072 cm^{-1}), (b) H_2O (1683 cm^{-1}), (c) NO_2/H_2O (1468 cm^{-1}), (d) NO (2050 cm^{-1}), (e) HCN (713 cm^{-1}) and (f) NH_3 (966 cm^{-1}).

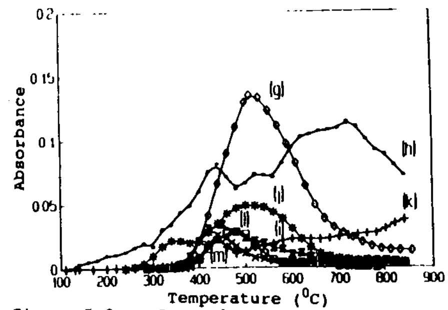

Figure 5-2. Gas release profile by TG-FTIR analysis for the low-chlorine coal IBC-106. (g) CH_4 (1304 cm^{-1}), (h) CO_2 (2360 cm^{-1}), (i) HCl/CH_4 (2962 cm^{-1}), (j) SO_2 (1360 cm^{-1}), (k) CO (2175 cm^{-1}), (l) C_2H_4 (950 cm^{-1}), and (m) C_3H_6 (912 cm^{-1}).

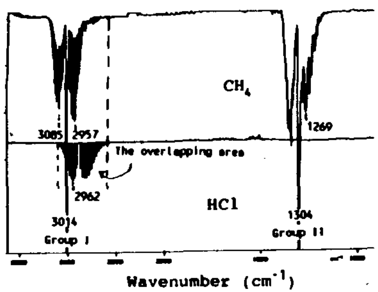

Figure 6. Comparison of The standard FTIR spectra of CH_4 and HCl.

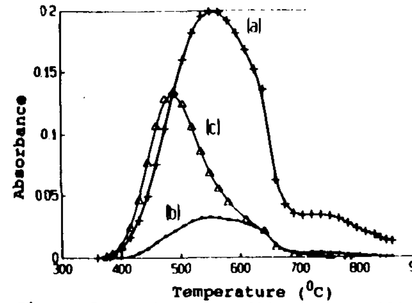

Figure 7. Release profile of CH_4 (1304 cm^{-1}, and 1269 cm^{-1}) and the HCl + CH_4 (2962 cm^{-1}) by TG-FTIR analysis of coal IBC-109. (a) CH_4 (1304 cm^{-1}), (b) CH_4 (1269 cm^{-1}), (c) HCl/CH_4 (2962 cm^{-1}).

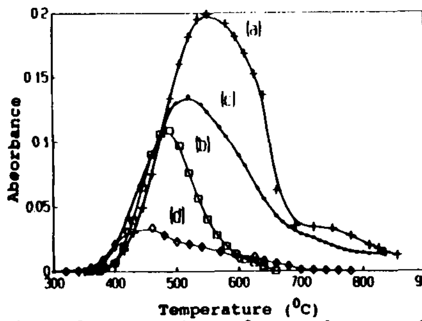

Figure 8. Comparison of gas release profiles of IBC-109 and IBC-106. (a) CH_4 (1304 cm^{-1}) from IBC-109, (b) HCl/CH_4 (2962 cm^{-1}) from IBC-109, (c) CH_4 (1304 cm^{-1}) from IBC-106 and (d) HCl/CH_4 (2962 cm^{-1}) from IBC-106.

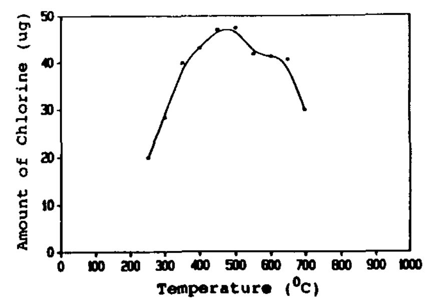

Figure 9. Gaseous chlorine release profile by IC analysis for the high-chlorine coal IBC-109.